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PLD-grown WO_3 nanostructures with ε-phase for gas sensor applications

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Abstract

Tungsten trioxide nanostructures, containing WO_3 ε-phase, were deposited by pulsed laser deposition (PLD) technique on *r*-plane Al_2O_3 substrates at room temperature and then annealed at 400 ºC. Partial oxygen pressure p(O_2) was varied from 0.1 mbar to 0.3 mbar. Structural characterization was carried out using XRD, Raman, and HRSEM measurements. Gas sensitivity responses of nanocrystalline sensors were measured for several gases including H_2S, H_2, NO_x, and CO. It was found that the sensor response was dependent on the phase and microstructure of WO_3 films.

Keywords: WO_3; ε-phase; nanostructures; gas sensors; PLD deposition

1. Introduction

WO_3 ceramics have been widely used for gas sensor applications. It shows good response to wide variety of gases [1,2]. The actual problems of using WO_3 in sensor applications are the lack of technological repeatability, demands for sensitivity increase, and decrease of crystalline size and operation temperature. WO_3 is well known as polymorphic material. WO_3 ε-phase is the most interesting one. It is stable at temperatures lower -53 ºC, but can also be stable due mechanical stress or size effect with crystallites in 5-10 nm size range at room temperature [3, 4]. Because of ferroelectric dipole moment, ε-phase WO_3 can have higher sensitivity and selectivity to various gas compounds. It was shown that ε-phase WO_3 films showed good sensitivity to acetone [1]. Thus, WO_3 nanostructures form a very promising group of material for gas sensors applications. PLD method is the most feasible technique for fabrication of WO_3 nanostructures and thin films with well defined properties. It was also reported that oxygen pressure influenced structural properties of WO_3 films such as stoichiometry and surface morphology [5]. In the present work we report new results on structural, optical, and sensitive properties of ε-phase WO_3 nanostructures. Gas sensitivity responses of nanocrystalline sensors were measured for several gases including H_2S, H_2, NO_x, and CO. The phase and microstructure of WO_3 films had a clear influence on the sensor response.

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2. Experimental

A pulsed XeCl-excimer laser (Lambda Physik COMPex 201, wavelength λ=308 nm) was used to ablate WO_3 target for tungsten trioxide thin film deposition. The repetition rate of the laser pulses was 5 Hz and the laser beam energy density at the target surface was 1.37 J/cm^2. The deposition was performed at room temperature. r-plane Al_2O_3 substrates were for thin films deposition. The substrate and target were placed parallel at the distance 35 mm. The deposition of tungsten trioxide nanostructures was provided at oxygen pressure 0.2 mbar. After deposition the obtained samples were annealed at 400 °C in air for 30 minutes. Phase identification of as deposited and annealed films was carried out by means of X-ray diffraction (XRD) (Philips MW 1380) instrumentation with CuKα radiation (λ=0.154 nm). The measurements were performed with a constant speed 1/8 °/min in the 2θ range of 20-40°. Raman spectra were measured (HORIBA Jobin Yvon LabRAM HR800) in the wavenumber range 50-1200 cm^{-1}. An Ar+ laser (λ=364 nm) was used for Raman excitation. HRSEM (FEI Helios Nova 600 NanoLab) experiments were carried out to characterize the nanoparticle size and surface morphology of the samples. Gas response of the resistive sensors was measured using Linkam THMSE 600 measurement stage with Linkam TMS94 temperature controller, and Signal Instrument Series 850 gas blender to control the gas flow connected to Linkam stage's gas feedthroughs.

3. Results

XRD patterns of two deposited and annealed samples are plotted in Fig.1. Both films present clear XRD peak sets at the 2θ angles of 23º-25º, 28º-30º, and 33º-36º corresponding to typical reflections of lattice plane groups of [(002), (020), (200)], [(120),(-112), (112)], and [(022),(202),(220)] of the monoclinic γ-WO_3, respectively. Since both ε-WO_3 and γ-WO_3 have monoclinic structures, thought different symmetries, $P2_1/n$ and Pc, respectively, and due to low signal-to-noise ratio, resolving and separation of the phases from the reflections of the data requires much more detailed work. However, films are clearly crystalline after annealing at 400 ºC, and, actually, the films deposited in the partial oxygen pressure $p(O_2)$ = 0.3 mbar are exhibiting crystallinity even after deposition at room temperature before annealing process.

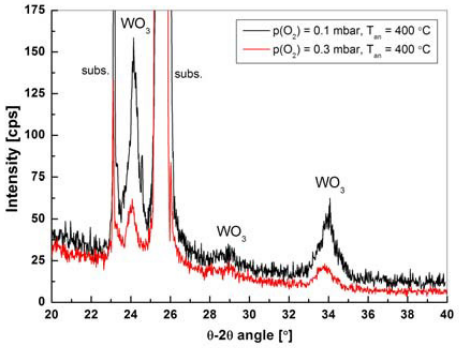

Fig. 1. XRD patterns of WO_3 nanostructures with γ- and ε-phase deposited at room temperature and in the partial oxygen pressure $p(O_2)$ of 0.1 and 0.3 mbar, and afterwards annealed at 400 ºC.

Raman spectra of corresponding nanostructured thin films as shown in Fig.1 are shown in Fig.2. In this case the different monoclinic phases are resolved more easily, and clear Raman peaks for both ε-phase (97, 205, 272, 305, 645, 690 cm^{-1}) and γ-phase (188, 331.6, 535 cm^{-1}) are seen in the spectra. The highest peak at around 808 cm^{-1} can be attributed for both phases. It can be seen from the patterns that the sample deposited in $p(O_2)$ = 0.3 mbar has clearly higher contents of ε-WO_3 phase, which is also reflected in XRD data at 2θ = 23º-25º in variation of group [(002), (020), (200)] reflection intensities.

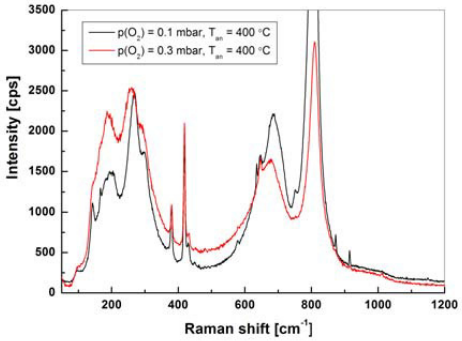

Fig. 2. Raman spectra of WO_3 nanostructures with ε-phase deposited at room temperature and afterwards annealed at 400 ºC.

HRSEM micrograph deposited in partial oxygen pressure of $p(O_2)$ = 0.3 mbar and afterwards annealed at 400 ºC is presented in Fig.3. Nanocrystalline structure of the samples is clearly seen as a porous collection of single or agglomerated nanocrystals with average grain size of ~50 nm. When the partial oxygen pressure of $p(O_2)$ used in depositions was decreased below 0.08 mbar, the nanoparticle nucleation in the ablation plume ceased, and the resulting samples represented more like uniform and flat thin films without nanoparticles. However, also in the case of *in situ* deposition with heated substrates at 400 ºC, ε-WO_3 phase could be detected by Raman spectroscopy when films were deposited in partial oxygen pressure of $p(O_2)$ = 0.1 mbar or higher. This is an evidence of nanocrystalline formation in laser ablation plume before the substrate surface, since the atomic species arriving the heated substrate surface tend to form a continuous thin film with epitaxial or large grained structures.

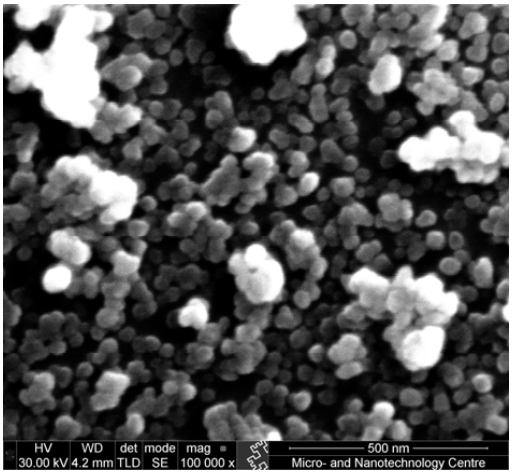

Fig. 3. HRSEM micrograph of WO_3 film with ε-phase deposited at room temperature and in the partial oxygen pressure $p(O_2)$ = 0.3 mbar, and afterwards annealed at 400 ºC.

As an example of the gas responses of nanocrystalline ε-WO_3 phase containing resistive sensors there is a H_2S response of an *in situ* deposited film with IDE platinum electrodes shown in Fig.4. The WO_3 thin film of the sensor was grown in PLD conditions with the substrate temperature of 400 ºC and in partial oxygen pressure of $p(O_2)$ = 0.1 mbar. High response with conductance ratio upto G_{gas}/G_o= 360 for H_2S concentration of 195 ppm were measured, whereas the detection limit was found to be less that 1 ppm.

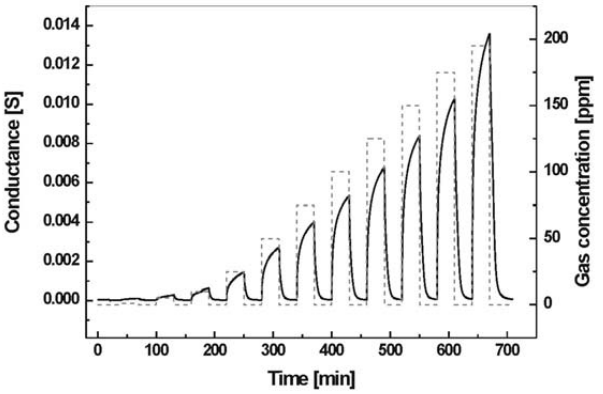

Fig. 4. Conductance response (black solid line) from 1 to 195 ppm of H_2S (dashed gray line) in synthetic air measured at 200 ºC of a WO_3 film with ε-phase deposited in *in situ* PLD conditions with substrate temperature of 400 ºC and in partial oxygen pressure of $p(O_2)$ = 0.1 mbar.

4. Summary

Tungsten trioxide nanoparticles with the average grain size of ~50 nm with ε-phase were grown using pulsed laser deposition technique with high partial oxygen pressure values over 0.1 mbar in the deposition chamber. XRD and, especially Raman spectroscopy measurements revealed the existence of the ferroelectric ε-WO_3 phase in the samples. Good gas response properties of resistive sensors were measured with the detection limit less than 1 ppm for H_2S, for example.

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References

[1] L. Wang, A. Teleki, S. E. Pratsinis, and P. I. Gouma. Ferroelectric WO_3 Nanoparticles for Acetone Selective Detection, *Journal of Chemistry of Materials* 2008, **20** 4794-4796.
[2] C. Zamani, O. Casals, T. Andreu, J. R. Morante, and A. Romano-Rodriguez. Detection of Amines with Chromium-doped WO_3 Mesoporous Material, *Sensors and Actuators B* 2009, **140** 557-562.
[3] S. Hayashi, H. Sugano, H. Arai, and K. Yamamoto. Phase Transitions in Gas-evaporated WO_3 Microcrystals: a Raman Study, *Journal of the Physical Society of Japan* 1992, **61** 916-923.
[4] M. Arai, S. Hayashi, and K.Yamamoto. Raman Studies of Phase Transitions in Gas-evaporated WO_3 Microcrystals, *Solid State Communications* 1990, **75** 613-616.